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(54) Improved phosphate-free detergent bleach compositions.

(57) Improved phosphate-free aluminosilicate built detergent bleach compositions having improved cleaning and stain-removal properties are disclosed. The compositions comprise at least one detergent-active material, from 20-35% water-insoluble aluminosilicate cation-exchange material, 2-5% by weight of an alkali metal nitrilotriacetate and 1-15% by weight of an organic solid peroxyacid compound.

The compositions are usable and effective for washing at temperatures of 40° C and below.

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IMPROVED PHOSPHATE-FREE DETERGENT BLEACH COMPOSITIONS

This invention relates to improved phosphate-free detergent bleach compositions. In particular it relates to aluminosilicate built laundry detergent bleach compositions having improved cleaning and stain-removal performances.

The role and value of phosphate detergency builders in laundry detergent compositions are well-known. In recent years, however, the use of phosphate builders, such as the alkali metal triphosphates, has come under scrutiny because of the suspicion that soluble phosphate species accelerate the eutrophication of water bodies. In a number of countries phosphate legislations have already forced detergent manufacturers to radically reduce the phosphate level of detergent compositions down to substantially zero. The need exists, therefore, for a built laundry detergent composition with zero phosphate level but which is comparable to a conventional triphosphate built composition in overall detergency effectiveness.

Furthermore, with the present trend to lower fabric washing temperatures, there is an incentive to improve on the formulations of detergent compositions so as to be effective at lower washing temperatures of e.g. 40 °C and below.

Water-insoluble aluminosilicates, commonly known as zeolites, have been used in detergent compositions as important alternative builders to phosphates (see, for example, GB-A-1429143; GB-A-1470250; GB-A-1504211; GB-A-1529454 and US-A-4064062).

It is known, however, that aluminosilicates, e.g. zeolites, are unable to duplicate the full range of builder functions demonstrated by phosphates. It is also known that in aluminosilicate built detergent compositions the performance of activated persalt bleach systems is significantly reduced.

In EP-A-70 079 it has been proposed to improve the activated persalt bleach performance in aluminosilicate built compositions by addition thereto of a nitrilotriacetic acid compound. The combined level of aluminosilicate and nitrilotriacetate, however, must be critical in order to achieve the desired effect.

EP-A-0181180 suggested an approach in that nitrilotriacetate is used with a lower level of zeolite but combined with a fairly substantial amount of a phosphate builder, which is unattractive and totally beyond the purpose of this invention.

A fundamental problem with activated persalt systems is that the peroxyacid is generated in situ from a perhydrolysis reaction between the activator and the persalt, which under practical conditions can give rise to yield difficulties.

Another, equally serious, drawback is that persalts are sensitive to catalase and peroxidase enzymes from soil which attack and decompose the persalt in competition with the activator/persalt perhydrolysis reaction, resulting in substantial loss of this bleach reactant.

It is an object of the present invention to provide an improved phosphate-free aluminosilicate built detergent composition having really effective cleaning and stain-removal performances at low wash temperatures of 40 °C and below, without the above drawbacks.

It has now been found that the above object can be achieved by using in the composition a solid organic peroxyacid compound as principal bleaching agent together with only a small amount of an alkali metal salt of nitrilotriacetic acid, i.e. 2-5% by weight.

Thus, according to the invention, there is provided a phosphate-free detergent bleach composition comprising at least one detergent-active material, from 20% to about 35% by weight of a water-insoluble aluminosilicate cation-exchange material, from 2% to 5% by weight of an alkali metal salt of nitrilotriacetic acid, which is characterized in that the composition contains from about 1% to about 15% by weight of a solid organic peroxyacid compound.

Preferably, the composition also includes an enzyme, particularly a proteolytic enzyme, in the usual amounts as known in the art.

Suitable proteolytic enzymes are normally solid, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the composition of the present invention. Examples of suitable proteolytic enxymes ar the subtilisins which are obtained from particular strains of B. subtilis and B. licheniformis, such as the commercially available subtilisins Maxatase® , as supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase® , as supplied by Novo Industri A/S, Copenhagen, Denmark.

Particularly suitable is a protease obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novo Industri A/S under the registered trade names Esperase® and Savinase ®. The preparation of these and analogous enzymes is described in British

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Patent Specification N° 1,243,784.

The amount of proteolytic enzymes used in the composition of the invention ranges from 0.001% to 10% by weight, preferably from 0.01% to 5% by weight, depending upon their activity. They are generally incorporated in the form of granules, prills or "marumes" in an amount such that the final washing product has a proteolytic activity of from about 2-20 Anson units per kilogram of final product.

The composition of the invention contains at least one detergent-active material which can be an organic soap or synthetic detergent surfactant material. Generally, from about 5% to 40% by weight of an organic, anionic, nonionic, amphoteric or zwitterionic detergent compound, soap, or mixtures thereof is included. Many suitable detergent-active compounds are commercially available and are fully described in literature, for example in US-A-4222905 and US-A-4239659 and in "Surface Active Agents and Detergents", Vol. I and II, by Schwartz, Perry and Berch.

The preferred detergent-active compounds which can be used are synthetic anionic, soap and nonionic compounds. The first-mentioned are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher aryl radicals. Examples of suitable synthetic, anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C_8-C_{18}) alcohols produced, for example, from tallow or coconut oil; sodium and potassium alkyl (C_9-C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10}-C_{15}) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those esters of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_9-C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralized with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphates such as those derived by reacting alpha-olefins (C_8-C_{20}) with sodium bisulphate and those derived by reacting paraffins with SO_2 and Cl_2 and then hydrolyzing with a base to produce a random sulphonate; olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10}-C_{20} alpha-olefins, with SO_3 and then neutralizing and hydrolyzing the reaction product. Suitable soaps are the alkali metal salts of long chain C_8-C_{22} fatty acids such as the sodium soaps of tallow, coconut oil, palmkernel oil, palm oil or hardened rapeseed oil fatty acids or mixtures thereof. The preferred anionic detergent compounds are sodium (C_{11}-C_{15}) alkyl benzene sulphonates and sodium (C_{16}-C_{18}) alkyl sulphates.

Examples of suitable nonionic detergent compounds which may be used include the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6-C_{22}) phenols, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule; the condensation products of aliphatic (C_8-C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally 6 to 30 EO, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylene diamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulphoxides.

Mixtures of detergent-active compounds, for example mixed anionic or mixed anionic and nonionic compounds, may be used in the detergent compositions, particularly in the latter case to provide controlled low sudsing properties. This is beneficial for compositions intended for use in suds- intolerant automatic washing machines.

Amounts of amphoteric or zwitterionic detergent-active compounds can also be used in the compositions of the invention, but this is not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic, detergent-active compounds are used, it is generally in small amounts in the compositions based on the much more commonly used synthetic anionic and/or nonionic detergent-active compounds.

The detergent composition of the invention also contains a water-insoluble aluminosilicate cation-exchange material in an amount of from 20% to 35% by weight.

The aluminosilicate can be crystalline or amorphous in character, preferred materials having the unit cell formula I

$$M_z [(AlO_2)_z (SiO_2)_y] xH_2O \qquad I$$

wherein M is a calcium-exchange cation, z and y are at least 6; the molar ratio of z to y is from about 1.0 to about 0.5 and x is at least 5, preferably from about 7.5 to about 276, more preferably from about 10 to about 264. The alumino-silicate materials are in hydrated form and are preferably crystalline containing from about 10% to about 28%, more preferably from about 18% to about 22% water.

The aluminosilicate ion-exchange materials are further characterized by a particle size diameter of from about 0.1 micron to about 10 microns, preferably from about 0.2 micron to about 4 microns. The term "particle size diameter" herein represents the average particle size diameter of a given ion-exchange

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material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope. The aluminosilicate ion-exchange materials herein are usually further characterized by their calcium ion- xchange capacity, which is at least about 200 mg. equivalent of $CaCO_3$ water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from about 300 mg eq./g to about 352 mg eq./g. The aluminosilicate ion-exchange materials herein are still further characterized by their calcium ion-exchange rate which is at least about 2 grains Ca^{++} gallon/minute/gallon of aluminosilicate (anhydrous basis), and generally lies within the range of from about 2 grains/gallon/minute/gram/gallon to about 6 grains/gallon/gram/gallon, based on calcium ion hardness. Optimum aluminosilicates for builder purposes exhibit a calcium ion-exchange rate of at least about 4 grains/gallon/minute/gram/gallon.

Aluminosilicate ion-exchange materials useful in the practice of this invention are commercially available and can be naturally occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion-exchange materials is discussed in US-A-3985669. Preferred synthetic crystalline aluminosilicate ion-exchange materials useful herein are available under the designations Zeolite A, Zeolite B, Zeolite X, Zeolite HS and mixtures thereof. In an especially preferred embodiment, the crystalline aluminosilicate ion-exchange material is Zeolite A and has the formula

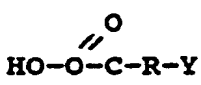
$Na_{12}[AlO_2)_{12}(SiO_2)_{12}]\ xH_2O$

wherein x is from about 20 to about 30, especially about 27. Zeolite X of formula $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]$.276 H_2O is also suitable, as well as Zeolite HS of formula $Na_6[(AlO_2)_6(SiO_2)_6]$ 7.5 H_2O).

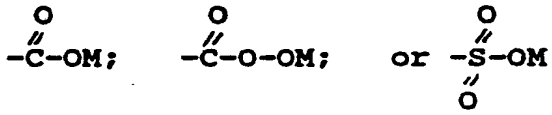
The nitrilotriacetic acid salt (measured in its preferred trisodium salt form) constitutes from 2 to 5% by weight of the composition. This range is important since no significant improvement in performance is observed with nitrilotriacetate levels of lower than 2% and higher than 5% by weight.

A further essential component of the compositions herein is from about 1% to about 15% by weight, preferably from 2% to 10% by weight of a solid organic peroxyacid compound. The organic peroxyacid compounds used in the present invention are solid at room temperature and should preferably have a melting point of at least 50° C.

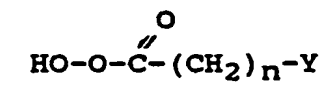
Such peroxyacid compounds are the organic peroxyacids and water-soluble salts thereof having the general formula:



wherein R is an alkylene or substituted alkylene group containing 1 to 20 carbon atoms or an arylene group containing from 6 to 8 carbon atoms, and Y is hydrogen, halogen, alkyl, aryl or any group which provides an anionic moiety in aqueous solution. Such Y groups can include, for example :

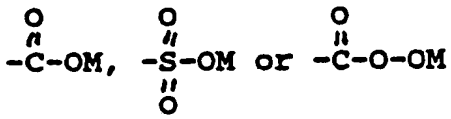


wherein M is H or a water-soluble, salt-forming cation. The organic peroxyacids and salts thereof usable in the present invention can contain either one, two or more peroxy groups and can be either aliphatic or aromatic. When the organic peroxyacid is aliphatic, the unsubstituted acid may have the general formula:



wherein Y can be H, $-CH_3$, $-CH_2Cl$,

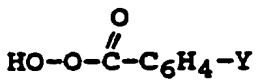
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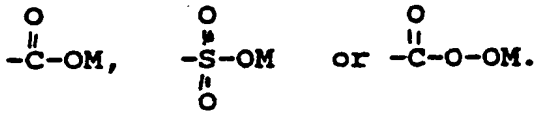
and n can be an integer from 6 to 20.

Peroxydodecanoic acids, peroxytetradecanoic acids and peroxyhexadecanoic acids are the most preferred compounds of this type, particularly 1,2-diperoxy-dodecanedioic acid, 1,14-diperoxytetradecanedioic acid and 1,16-diperoxyhexadecanedioic acid. Examples of other preferred compounds of this type are diperoxyazelaic acid, diperoxyadipic acid and diperoxysebacic acid.

When the organic peroxyacid is aromatic, the unsubstituted acid may have the general formula:



wherein Y is, for example, hydrogen, halogen, alkyl,



The percarboxy and Y groupings can be in any relative position around the aromatic ring. The ring and/or Y group (if alkyl) can contain any non-interfering substituents such as halogen or sulphonate groups. Examples of suitable aromatic peroxyacids and salts thereof include monoperoxyphthalic acid, diperoxyterephthalic acid, 4-cholorodiperoxyphthalic acid, diperoxyisophthalic acid, m-chloroperoxybenzoic acid, p-nitroperoxybenzoic acic, and peroxy-alpha-napthoic acid. A preferred aromatic peroxyacid is diperoxyisophthalic acid.

A particularly preferred peroxyacid for use in the present invention is 1,12-diperoxydodecanedioic acid (DPDA).

Suitable and preferred salts of peroxyacids are the magnesium salts of peroxycarboxylic acids, such as are described in EP-A-0 105 689, EP-A-0 195 597 and EP-A-0 195 663.

Apart from the components already mentioned, the detergent composition herein can contain any of the conventional additives and adjuncts in the amounts in which such materials are normally employed in fabric washing compositions. Examples of such additives include lather boosters such as alkanolamides, particularly the monoethanolamides derived from palmkernel and coconut fatty acids; lather depressants such as alkyl phosphates, silicones and waxes; anti- redeposition agents such as sodium carboxymethyl cellulose (SCMC), polyvinyl pyrrolidone (PVP) and the cellulose ethers such as methylcellulose and ethyl hydroxyethyl cellulose; stabilizers such as ethylene diamine tetraacetate, ethylene diamine tetramethylene phosphonate and diethylene triamine penta-methylene phosphonate; fabric softening agents; inorganic salts such as sodium sulphate and sodium carbonate; and - usually present in very minor amounts - fluorescent agents, perfumes, germicides and colourants and other enzymes such as amylases, lipases and possibly also cellulases. Polycarboxylate polymers, though not essential, may also be included as desired in amounts of e.g. from about 0.5% to 6% by weight of the total composition. The polycarboxylate polymers herein are preferably selected from co-polymeric polycarboxylic acids and their salts derived from an unsaturated polycarboxylic acid such as maleic acid, citraconic acid, itaconic acid or mesaconic acid as a first monomer and ethylene, methyl vinyl ether, acrylic acid or metacrylic acid as a second monomer, the co-polymer comprising at least about 10 mole%, preferably at least about 20 mole% of polycarboxylic acid units and having weight average molecular weights of at least about 10,000, preferably at least about 30,000; homopolyacrylates and homopolymethacrylates having a weight average molecular weight of from about 1000 to about 80,000, preferably from about 5000 to about 50,000; and mixtures thereof.

Additionally, th compositions may optionally include an inorganic peroxide compound, such as the alkali metal perborates, percarbonates, perphosphates and persilicates, the perborates, particularly sodium perborate tetra- and monohydrates, being preferred because of their commercial availability. If added, they may be present in an amount of not more than 20% by weight, preferably not more than 15% by weight of

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the final composition. The addition of inorganic peroxide compounds may be desirable for improving high-temperatur performanc .

The detergent compositions of the invention are preferably presented in free-flowing particulate, e.g. powdered or granular form, and can be produced by any of the known techniques commonly employed in the manufacture of such washing compositions, but preferably by spray-drying an aqueous slurry comprising the surfactant(s) and the alumino-silicate and the nitrilotriacetic acid salt to form a detergent base powder, to which the heat-sensitive ingredients are added, including the organic peroxyacid, peroxide compound, enzymes and optionally some other ingredients as conveniently desirable. It is preferred that the process used to form the compositions should result in a product having a moisture content of up to about 15%, more preferably from about 7% to about 14% by weight. The detergent bleach compositions of the invention are generally alkaline and will advantageously have a pH (at 2-10 g/l) in aqueous solution of from about 8-11.

The invention will now be illustrated by the following non-limiting Examples.

Example I

The following particulate non-phosphate detergent composition was prepared by spray-drying an aqueous detergent slurry to form a detergent base powder composition (A).

Composition A	Parts by weight
Sodium linear alkylbenzene sulphonate	9.0
Fatty alcohol-7 ethoxylate	4.0
Maleic acid/acrylic acid copolymer (Sokalan ® CP5 ex BASF)	4.0
Sodium aluminosilicate (Zeolite A)	24.0
Sodium sulphate (anhydrous)	6.8
Sodium carboxymethyl cellulose	0.5
Sodium ethylenediamine tetraacetate (EDTA)	0.2
Water and fluorescer (0.13)	7.6

Washing experiments were carried out with this composition including 3% by weight of DPDA without and with added trisodium nitrilotriacetate (NTA) at various levels of 2%, 3%, 5% and 10% by weight in 30 minutes' Tergotometer washes using a dosage of 6 grams/litre in 24° FH water at 40° C, buffered at pH 8.5.

The bleaching properties on tea and red-wine stains were measured and the results are given in Table I.

Table I

	ΔR values	
	Tea	Wine
Composition A + 0% NTA	10.6	24.6
" + 2% NTA	12.0	26.7
" + 3% NTA	11.5	27.5
" + 5% NTA	11.4	28.3
" + 10% NTA	10.7	25.3

An overall enhancement of bleaching performance at 40° C of the detergent compositions comprising 2-5% NTA is clearly shown.

Addition of 10% NTA does not appear to give bleach performances that differ significantly from a zero NTA addition.

Example II

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The experiments of Example I were repeated using the following detergent powder compositions C and C¹.

Composition C	Parts by weight
Sodium dodecyl benzene sulphonate	9.0
Fatty alcohol-7-ethoxylate	4.0
Zeolite	24.0
Maleic acid/acrylic acid copolymer (Sokalan CP5 ex BASF)	4.0
Sodium carboxymethyl cellulose	0.5
EDTA	0.2
Sodium sulphate	44.1
Fluorescer	0.2
Water	8.0
Diperoxy dodecanedioic acid	6.0
Proteolytic enzyme (Savinase ex NOVO)	0.5

Composition C¹ is Composition C without Sokalan CP5 co-polymer.
The results are given in the following Table.

Table 2

	ΔR-values			
	Tea	Wine	Detergency	Protein stains
Composition C	6.9	21.6	21.5	27.6
" + 5% NTA	17.2	35.7	24.7	30.5
Composition C¹	6.4	21.2	21.8	17.2
+ 5% NTA	18.2	36.5	24.0	19.8

The results show again the excellent overall cleaning and bleaching performances of the compositions according to the invention at 40° C.

Example III

The washing and bleaching experiments of Example I were repeated using the following base powder combination without and with 5% NTA.

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Copmosition D_1	Parts by w ight
Sodium linear C_{12}-alkylbenzene sulphonate	9.0
C_{13}-C_{15}-alcohol-7 ethoxylate	1.5
Maleic acid/acrylic acid copolymer	4.0
Sodium aluminosilicate (Zeolite A)	24.0
Sodium sulphate	0.3
Sodium carboxymethyl cellulose	0.5
Sodium EDTA	0.2
Sodium carbonate	2.0
Water and fluorescer (0.13)	7.6
Composition D_2	
Sodium perborate monohydrate	8.0
Anti-foaming agent	2.5
Proteolytic enzyme (Savinase ex NOVO)	0.5
Diperoxydodecanoic acid (DPDA)	6.0
Sodium sulphate	33.9

These compositions may be presented in a dual compartment pack wherein the NTA is included, for example in the D_1 composition compartment.

The results are shown in the following Table 3.

Table 3

	ΔR-values			
	Tea	Wine	Detergency	Protein stains
1) Composition D_1/D_2	8.0	25.4	22.3	17.0
2) " D_1/D_2 + 5% NTA	16.8	37.0	23.4	25.9

Again the results show a clear difference in performance between the composition of the invention 2) and the composition outside the invention 1).

Claims

1. A phosphate-free detergent bleach composition comprising at least one detergent-active material, from 20% to about 35% by weight of a water-insoluble aluminosilicate cation-exchange material, and from 2% to 5% by weight of an alkali metal salt of nitrilotriacetic acid, characterized in that the composition contains from about 1% to about 15% by weight of a solid organic peroxyacid compound.

2. A composition according to Claim 1, characterized in that it further comprises a proteolytic enzyme in an amount such that the composition has proteolytic activity from about 2 to 20 Anson units per kilogram of product.

3. A composition according to Claim 1 or 2, characterized in that said solid peroxyacid compound is present in an amount of from 2% to 10% by weight of the composition.

4. A composition according to Claim 1, 2 or 3, characterized in that said solid peroxyacid compound is 1, 12-diperoxy dodecanedioic acid.

5. A composition according to Claim 1, 2 or 3, characterized in that said solid peroxyacid compound is a magnesium salt of peroxycarboxylic acid.

6. A composition according to any of the above Claims 1-5, characterized in that said alkali metal salt of nitrilotriacetic acid is trisodium nitrilotriacetate.

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7. A composition according to any of the above Claims 1-6, characterized in that it further comprises an inorganic peroxide compound selected from sodium perborate tetra- and monohydrate in an amount of not more than 15% by weight of the total composition.

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EUROPEAN SEARCH REPORT

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EP 88 20 2354

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A,D	EP-A-0070079 (UNILEVER NV.) * the whole document *	1	C11D3/395 C11D3/12 C11D3/33
A	EP-A-0103416 (THE PROCTER & GAMBLE COMPANY) * the whole document *	1, 7	
A	GB-A-2178754 (COLGATE PALMOLIVE COMPANY) * the whole document *	1-2	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30 AUGUST 1990	TETAZ F.C.E.

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